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# Annotated bibliography of 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid

## **Abstract**

In the following annotated bibliography on 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid, the references are listed in chronological order, and are numbered consecutively.

## **Disciplines**

Chemistry

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CHEMISTRY—GENERAL

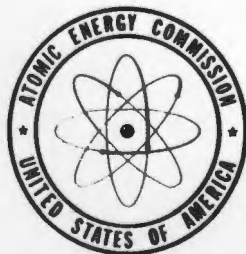
UNITED STATES ATOMIC ENERGY COMMISSION

ANNOTATED BIBLIOGRAPHY OF 2-(2-HYDROXY-3,6-DISULFO-1-NAPHTHYLAZO)-  
BENZENEARSONIC ACID

By  
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Gerald L. Weiss

July 3, 1957

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Ames, Iowa



Technical Information Service Extension, Oak Ridge, Tenn.

**F. H. Spedding, Director, Ames Laboratory.**

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## ANNOTATED BIBLIOGRAPHY OF

## 2-(2-HYDROXY-3,6-DISULFO-1-NAPHTHYLAZO)-BENZENEARSONIC ACID

Charles V. Banks and Gerald L. Weiss

## Introduction

In the following annotated bibliography on 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid, the references are listed in chronological order, and are numbered consecutively.

Many names have been given to the reagent; throughout the bibliography each worker's name for the compound has been retained. The reagent can be found under the following names: 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid, o-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid, 1-(2-arsonobenzeneazo)-2-naphthol-3,6-disulfonic acid, 1-(2-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, Thoron, Thorin, Thoronol, Naphtharson and APANS.

It is hoped that this bibliography will be of some use to those interested in the preparation and analytical applications of 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid.

1940

1. Kuznetsov, V. I., "Color Reactions for Thorium, Uranium and Other Elements," Zhur. Obshchei Khim., 10, 1512 (1940) [C. A., 37, 845 (1943)].

Treatment of thorium, uranium and other elements with 2-(o-arsonophenylazo)-p-cresol, 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, 1-(o-arsonophenylazo)-2-naphthol-6,8-disulfonic acid, and 3-(o-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid in (a) neutral or slightly acid solution, (b) in the presence of rare earths gave different colors that were tabulated.

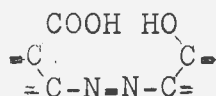
The colors obtained for 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid are as follows:

Elements	Neutral or Slightly Acid	HCl
Rare Earths	orange	orange
Zr	orange	orange
Sn(IV)	orange-yellow	orange-yellow
Th	crimson-pink	crimson-pink
Cb	--	pink-orange
Ta	--	pink-orange
U	pink-orange	orange-yellow

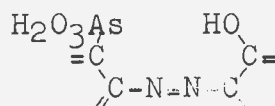
### 1941

2. Kuznetsov, V. I., "Color Reactions of Thorium, Uranium and Other Elements," Compt. rend. acad. sci. U. R. S. S., 31, 898 (1941) C. A., 37, 845 (2) (1943) 7.

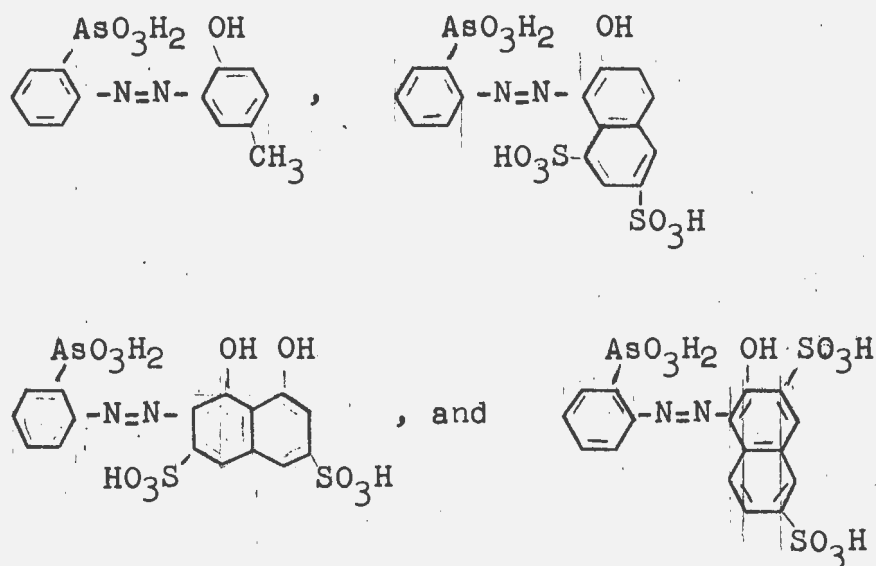
Azo compounds with hydroxy groups in the ortho position to the azo group have, to a certain degree, mordant properties. The metallic compounds lead to a sharp change in coloration. Their non-specific action hinders the wide uses of orthohydroxyazo compounds as analytical reagents. The presence of a carboxyl group ortho to the azo group



considerably favors the change in color, but it is non-selective. Orthohydroxyazo compounds, having an arsono group in the second ortho position to the azo group



are selective precipitating agents. In basic media Th, Zr, Hf, Nb, Ta, Ti, U and rare earths are precipitated. The colors developed with each of the above elements are listed for the following:



The sensitivity of these colored reagents to color changes is 1 part in a million.

1944

3. Kuznetsov, V. I., "Color Reaction of Thorium," Zhur. Obshchei Khim., 14, 914 (1944) C. A., 39, 4561 (1945) 7.

The 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid serves to detect thorium in the presence of rare earths and other elements by the formation of a strawberry-red precipitate.

Titanium gives an indistinct orange-red color, zirconium interferes somewhat, and Fe(III) interferes if present in more than a 100-200 ratio.

The reagent is prepared from o-aminobenzenearsonic acid in dilute HCl with sodium salt of 2-naphthol-3,6-disulfonic acid. Diazo coupling of o-aminobenzenearsonic acid with 2-naphthol-6,8-disulfonic acid yields products which also give analogous color reactions, but are not as effective as the above reagent.

1945

4. Kuznetsov, V. I., "Increase of Sharpness of Color Tests with Organic Reagents," Doklady Akad. Nauk S. S. S. R., 50, 233 (1945); Compt. rend. acad. sci. U. R. S. S., 50, 233 (1945) C. A., 43, 4174e (1949) 7.

The color formation in organic reagents is reviewed on the basis of the internal ionization in molecules having distinct dipole character. Known reagents are readily improved by increasing the dipole effect by the use of electrically "opposite" groups. Comparison of color tests with reagents having  $\text{NH}_2$ , H, or  $\text{NO}_2$  groups in comparable positions gives additional proof. 4-Nitro-2-arsonophenylazo-2-naphthol-3,6-disulfonic acid gives red-orange with thorium in hydrochloric acid solution and orange-pink with uranium(VI) in sodium acetate solution. This reagent, without the  $\text{NO}_2$  group, gives strawberry-pink and orange-pink, respectively. 4-Amino-2-arsonophenylazo-2-naphthol-3,6-disulfonic acid gives bright violet and blue-violet, respectively.

1948

5. Kuznetsov, V. I., "Color Reaction on Lithium," Zhur. Anal. Khim., 3, 295 (1948) C. A., 43, 8954c (1949) 7.

Visual tests are described in which 12 organic compounds were used that gave colored complexes with lithium. It is stated that 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid (Thoron) forms an orange-colored complex with lithium in a strongly alkaline media. The author compared, visually in daylight, the color of solutions that contained approximately 2% of lithium per ml., 3 drops of a 0.1% solution of Thoron and 2 to 3 drops of a 20% potassium hydroxide solution with the color of a solution that contained only Thoron.

1949

6. Thomason, P. F., Perry, M. A. and Byerly, W. M., "Determination of Micrograms of Thorium," Anal. Chem., 21, 1239 (1949); cf., USAEC Report ORNL-90 (1948).

A colorimetric method for determining thorium in the range 0.5-80 micrograms has been developed, using



1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid. Uranium and the rare earths do not interfere in amounts less than 1000 micrograms and interference from Fe(III) can be lessened by reduction to the Fe(II) state.

7. Sherman, A., Reed, S. A., Byrd, C. H. and Banks, C. V., "Preparation of the Disodium Salt of 1-(o-Arsonophenylazo)-2-naphthol-3,6-disulfonic Acid (Thoron)," USAEC Reports ISC-26 (1948) and AECD-2565 (1949).

A detailed 3-step procedure for synthesis of disodium salt of "Thoron" is presented: (a) the coupling of o-nitroaniline with disodium hydrogen arsenite by the Bart reaction to form 2-nitrophenylarsonic acid, (b) the reduction of 2-nitrophenylarsonic acid to 2-aminophenylarsonic acid with iron(II) chloride and (c) the coupling of the 2-aminophenylarsonic acid with 2-naphthol-3,6-disulfonic acid (R-salt) by the Griess reaction.

#### 1950

8. Kuznetsov, V. I., "The Effect of pH on the Color of Internally Complex and Cyclic Salts," Zhur. Obschei Khim., 20, 816 (1950); J. Gen. Chem. U. S. S. R., 20, 853 (1950) /C. A., 45, 1453c (1951); C. A., 46, 19081 (1952) 7.

This article discusses some of the causes for color change in many compounds, of which Thoron is one example.

The color of solutions of inner coordination salts and of cyclic salts in general, formed with colored reagents, is due chiefly to the state of their intramolecular dissociation.

In many cases, if the pH values are suitable, the colors of solutions of the cyclic salts of various elements are close to the combined colors of solutions of the original reagents. The colors of a solution at some pH may be reproduced by adding the colors of the ionized and nonionized forms of the reagent. Different

colors of the ionized forms (phenolates, azo salt) are observed when the reagents are dissolved in media with different pH, and a different color may be observed in concentrated sulfuric acid than in another acid of the same pH.

In some cyclic salts, the effect of several atomic groups upon the color may all coincide though their effect is not additive in solutions of the pure reagent, nor can they be reproduced by adding the colors of its different ionized and nonionized forms.

The color of a solution of the cyclic salt, formed by a metallic ion exhibiting chromophore activity and an uncolored reagent, approaches the color of the metal hydroxide as the pH increases. This is due to diminution of the intramolecular dissociation of the cyclic salts and a probable simplification of their composition, resulting in partial decomposition of more complex coordination compounds.

With a colored reagent the color approaches the color of the nonionized form of the reagent as the pH is increased.

#### 1951

9. Nikolaev, A. V. and Sorokina, A. A., "Colorimetric Determination of Lithium," Doklady Akad. Nauk S. S. S. R., 77, 427 (1951) [C. A., 45, 7913a (1951)].

Nikolaev extended the work of Kuznetsov to determine, by visual comparison, 0 to 25.0 mg. lithium in a 50-ml. volume. The author states that this method suffers from the difficulty of matching colors, "which can be done only in daylight."

#### 1952

10. Horton, A. D., Thomason, P. F. and Miller, F. J., "Spectrophotometric Determination of Inorganic Fluoride," Anal. Chem., 24, 548 (1952); cf., USAEC Report ORNL-686 (1950).

The fluoride ion diminishes the color produced when Thoron reagent, 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, is added to thorium nitrate solution.

This leads to the development of a spectrophotometric determination of microgram quantities of fluorides (0 to 50 micrograms) with an accuracy of  $\pm 4\%$ , and a mean standard deviation of 0.85 microgram. Separation of the fluoride from the interfering ions is improved by an automatically controlled steam-distillation apparatus. Total time for an analysis is about 40 minutes.

11. Mayer, A. and Bradshaw, G., "The Absorptiometric Determination of Thorium in Magnesium-Base Alloys by 1-(o-Arsonophenylazo)-2-naphthol-3,6-disulfonic Acid," Analyst, 77, 154 (1952).

A method for the determination of thorium in magnesium-base alloys is described. If zirconium is present, thorium is separated by precipitation as the oxalate. None of the other elements normally present in magnesium alloys interfere. The method gives results correct to within 0.2% in the range 0.2% to 5%. It can be applied to samples with widely differing thorium content and is reasonably rapid.

Thorium is separated from magnesium by an ammonium hydroxide precipitation; separation from zirconium is then effected by precipitating thorium and rare earths as oxalates. The oxalates are converted to perchlorates and thorium is determined absorptiometrically, without removing rare earths with 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid (APANS, Thornol).

12. Taylor, A. E. and Dillon, R. I., "Determination of Microgram Quantities of Thorium in Water," Anal. Chem., 24, 1624 (1952).

Thorium was concentrated by precipitation of thorium as an oxalate with calcium as a carrier, under controlled conditions of pH. By heating, the oxalate was converted to carbonate, which was then dissolved in hydrochloric acid. The determination of the concentration of thorium was performed utilizing 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid. A Beckman D. U. spectrophotometer was used for the measurements.

Calcium ion concentration variations have a small linear effect upon the absorbancy of the solution, and no effect on the linearity of the relation between the thorium concentration and the absorbancy of the solution.

Ferric iron was the only substance that caused interference. This interference was eliminated by reduction to the ferrous state with 1 ml. of 10% hydroxylamine.

### 1953

13. Byrd, Carol H., "Spectrophotometric Determination of Thorium with the Trisodium Salt of 2-(2-Hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic Acid and some Properties of the Complexes Involved," Ph. D. Thesis, Iowa State College Library, Ames, Iowa.

In the thesis some properties of the complexes between thorin and thorium are examined.

By variation of the pH one can detect two effects on the Thorin molecule through a change in the absorption spectra. As the pH is raised, the hydrogens are removed from the arsono group and the equilibrium is shifted to the hydrozone form. At pH values of 7.0 and above, the molecule becomes unstable. Maximum difference between the reagent and complex absorption occurs at a pH of around 1.00, in the region 540 m $\mu$ .

A time study on a series of solutions prepared according to Job's method of continuous variations was carried out. The concentrations employed were  $10^{-5}$  M to  $10^{-4}$  M. On standing the absorbance increased, levelled off, and a precipitate developed after several days. Various plots showed that there were several complexes formed. Dissociation constants did not fit the several postulated equilibria.

The optimum conditions for the spectrophotometric method were established. Methods for determining 20 to 2000  $\mu$ g. thoria were developed. The principal cation interferences are iron(III), bismuth(III), rare earths, uranium(IV) and (VI), titanium(IV) and chromium(IV). The principal anion interferences are phosphate and sulfate.

A rapid method for the determination of thorium in monazite sands was developed. The procedure involves (1) fusion of the sand with potassium hydrogen fluoride and separation of the insoluble rare earth and thorium fluorides by centrifugal action, (2) solution of the fluorides in a saturated aluminum nitrate solution acidified with nitric acid, (3) extraction of the thorium into mesityl oxide and re-extraction into water, and (4) the spectrophotometric determination of the thorium in the extract with Thorin.

14. Banks, C. V. and Byrd, C. H., "Spectrophotometric Determination of Thorium in Monazite Sands," Anal. Chem., 25, 416 (1953).

A method is described for the rapid determination of thorium in monazite sands. The procedure involves fusing the sand with potassium bifluoride and separating the insoluble rare earth and thorium fluorides by centrifuging, dissolving these fluorides in a saturated solution of aluminum nitrate, extracting the thorium into mesityl oxide, then stripping it from this solution with water and concluding the determination by a spectrophotometric analysis of the resulting thorium solution. The disodium salt of 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid was used as the color-forming reagent.

The average difference between the reported amounts of thorium in the samples used and the amounts of thorium determined by this method was + 0.14%. The average precision obtained was  $\pm 0.03\%$ . This method has the advantages of greater speed and fewer separations.

15. Banks, C. V., Klingman, D. W. and Byrd, C. H., "Spectrophotometric Determination of Thorium in Black Sands," Anal. Chem., 25, 992 (1953).

The spectrophotometric determination of thorium in black sands includes the sample preparation, sample decomposition, separation and solution of fluorides, and extraction with mesityl oxide.

The preparation and decomposition consisted of grinding the samples to 200 mesh, fusing with potassium bifluoride and digesting with dilute hydrofluoric acid under infrared heating lamps.

The separation and solution of the fluorides consisted of a centrifuge method by which the supernatant liquid and 16% hydrofluoric acid were poured off. The residue was dissolved with aluminum nitrate 9-hydrate.

Thorium was extracted from the solution of fluoaluminates with mesityl oxide.

After separation of the mesityl oxide, thorium was stripped with water.

With Thorin as the indicator, the thorium was determined with a Beckman Model DU spectrophotometer.

16. Margerum, D. W., Byrd, C. H., Reed, S. A. and Banks, C. V., "Preparation and Properties of 2-(2-Hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic Acid (Thorin) Analytical Reagent for Thorium," Anal. Chem., 25, 1219 (1953).

A detailed procedure for the synthesis of Thorin was given. The synthesis involved three steps: (a) the coupling of 2-nitroaniline with disodium hydrogen arsenite by the Bart reaction to form 2-nitrobenzenearsonic acid, (b) the reduction of 2-nitrobenzenearsonic acid to 2-aminobenzenearsonic acid with ferrous chloride and (c) the coupling of the 2-aminobenzenearsonic acid with the disodium salt of 2-naphthol-3,6-disulfonic acid (R-salt) by the Griess reaction.

Dissociation constants of the acids were determined. The constants  $pK_3 = 3.7$  and  $pK_4 = 8.3$  for the arsonic hydrogens were determined potentiometrically.

The constant  $pK = 11.8$  for the naphtholic hydrogen was determined spectrophotometrically.

17. Horton, A. D., "Spectrophotometric Determination of Zirconium," Anal. Chem., 25, 1331 (1953).

The determination of zirconium with the use of Thoron as a spectrophotometric reagent is discussed in the article. The method covers a range of .10  $\mu$  to 100  $\mu$  of zirconium with a precision within 5.7% in the 10  $\mu$  range, and 2.9% in the 100  $\mu$  range.

The development of the color of the complex was complete after 2 hours, and is stable for at least 6 hours.

Hafnium is identical to zirconium in its reaction with Thoron, and in its adsorption characteristics. One microgram of zirconium is spectrophotometrically equivalent to 2.1 of hafnium (1 mole of zirconium = 1.05 moles of hafnium).

18. Thomason, P. F., "Spectrophotometric Determination of Lithium," USAEC Report ORNL-1521 (1953).

A spectrophotometric method for determining amounts of lithium has been developed that uses 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid (Thoron) as the chromogenic reagent in an alkaline solution of water and acetone. Copper and magnesium cause little interference when present in amounts less than ten times the amount of lithium. Sodium can be tolerated in amounts up to fifty times the amount of lithium. Potassium does not interfere; in fact, a potassium hydroxide solution is used as one of the reagents in the procedure. The results of the analysis of lithium chloride solutions have shown that the accuracy of the method is of the order of  $\pm 3\%$ .

#### 1954

19. Dalton, J. C. and Thomson, S. J., "Recent Studies on Iron Meteorites. V. Improved Methods for the Isolation of Uranium and Thorium From Meteorites," Geochim. et Cosmochim. Acta, 5, 74 (1954) C. A., 48, 7503a (1954) 7.

A method is described for the separation of  $10^{-8}$  g. quantities of thorium from solutions of iron meteorites. 1-(o-Arsonophenylazo)-2-naphthol-3,6-disulfonic acid was used as a precipitant with zirconium as a carrier. The uranium present has been shown to remain quantitatively in solution. Two methods are described for the recovery of uranium in a sufficiently pure state for fluorimetry: these are solvent extraction and paper chromatography.

A U-233 tracer technique, combined with fluorimetry, has allowed estimates to be made of meteoritic uranium.

20. Ford, J. J. and Fritz, J. S., "Titrimetric Determination of Thorium," USAEC Report ISC-520 (1954).

Thorin was tried as a color indicator but Alizarin Red was used because it had fewer cation interferences.

21. Fritz, J. S. and Freeland, M. Q., "Direct Titrimetric Determination of Sulfate," Anal. Chem., 26, 1593 (1954).

In the determination of sulfate, Alizarin Red S (sodium alizarin 3-sulfonate) was used as the negative ion adsorption indicator. It was suggested that o-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid disodium salt could be used in place of Alizarin Red S. Thorin exhibits a sharper end-point than Alizarin Red S. Thorin changes from yellow to pink. The sharpest end-point is around pH 2-3, and the end-point is stoichiometric at pH 1.5-3.5.

A mixture of water and alcohol was used as the solvent because this type of solvent develops sharper end-points.

22. Kuznetsov, V. I., "Color Reactions of Bivalent Chromium," Doklady Akad. Nauk S. S. S. R., 95, 547 (1954)  
[C. A., 48, 8692h (1954)].

Some specific color reactions of Cr(II) are believed to be due to the reducing power of Cr(II) followed by complexation of the resulting Cr(III).

Cr(II) seems to form many colored compounds when Cr-O- and Cr-N= bonds are present. Thorin is one of the many compounds that gives a color change upon the addition of Cr(II). The color change is from a yellow-colored reagent to a rose-colored complex.



1955

23. Fritz, J. S. and Yamamura, S. S., "Rapid Microtitration of Sulfate," Anal. Chem., 27, 1461 (1955).

Small concentrations of sulfate can be determined by a direct titration with 0.005M. barium perchlorate with Thorin [2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid] as the indicator. The titration is carried out in 80% alcohol (ethyl alcohol, 2 propanol, or methanol by volume). The pH range is adjusted to 2.5 to 4.0. The end-point is sharp and equilibrium is rapidly attained. Some interfering ions must be removed. Anions such as phosphate can be removed by precipitation with magnesium carbonate, and the sulfite ion can be removed by oxidation with iodine. Cations can be removed with cation exchange columns.

The titrimetric microprocedure has been adapted to the determination of sulfate in raw water, treated city water, and in boiler water.

1956

24. Grimaldi, F. S. and Fletcher, M. H., "Thoron-Tartaric Acid Systems for Spectrophotometric Determination of Thorium," Anal. Chem., 28, 812 (1956).

This study describes the use of tartaric acid as a masking reagent for zirconium. Three tartaric acid-thoron systems developed for the determination of thorium differ with respect to the concentrations of Thoron and tartaric acid.

The Thoron concentration in the first system was one-half that in the second system, and the third system used mesotartaric acid instead of the common d-tartaric acid used in the first two systems. Mesotartaric acid is the most effective in masking zirconium. The method was used on thorium ores and a dilution method is described for the direct determination of thorium in monazite sands.

25. Miller, F. J. and Thomason, P. F., "Automatic Photometric Titration of Sulfate," USAEC Report ORNL-2040 (1956).

Amounts of sulfate in the range 0.048 to 17 mg. have been titrated with good precision (Standard

Error at 95% Probability Level is 0.19% to 0.16%). The titration with standard  $\text{Ba}(\text{ClO}_4)_2$  solutions by use of 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid (Thoron) as an adsorption indicator was adapted for automatic photometric titration. A simple titration-cell assembly was devised that incorporated an interference filter (10 m $\mu$  wide at 515 m $\mu$ ) and a photo tube (RCA5652). This cell was used in conjunction with the ORNL model Q-945 automatic titrator.

26. Thomason, P. F., "Spectrophotometric Determination of Lithium," Anal. Chem., 28, 1527 (1956).

Microgram amounts of lithium can be determined spectrophotometrically by using o-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid as the chromogenic agent in a potassium hydroxide solution of water and acetone. Calcium and magnesium cause little interference in amounts up to 50 times the amount of lithium. Results on determinations of lithium chloride solutions show an accuracy within the order of  $\pm 3\%$  when compared to results of a flame photometer.

27. Rády, G. and Erdey, L., "Complexometric Bismuth Determination," Z. anal. Chem., 152, 253 (1956) C. A., 51, 3356e (1957) 7.

Two drops of 0.5% sodium salt of 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid will permit the titration of bismuth in a weak nitric acid solution with versene. The resulting red coloration disappears at the equivalence point with the dissolving of bismuth(III) complex in the pH range 1 to 3 to give a clear yellow solution.

Bismuth in the range of 2 to 200 mg. can be determined with an average error of  $\pm 0.3\%$ . The precision is  $\pm 0.1\%$ .

The following metal ions will interfere with the determination: thorium(III), cerium(IV), zirconium(IV), lanthanum(III), uranium(VI) and iron(III). The interference of iron(III) can be removed by a reduction with ascorbic acid. The anions that interfere are phosphate, chloride, sulfate and fluoride.

28. Clinch, J., "The Colorimetric Determination of Thorium With 1-(o-Arsonophenylazo)-2-naphthyl-3,6-disulfonic Acid," Anal. Chim. Acta, 14, 162 (1956) C. A., 51, 2462d (1957) 7.

This article mentions the effect of temperature on the stability of the thorium complex, and the effect of pH on the development of the color.

The effect of interfering cations, and anions are discussed. The interfering cations are lanthanons, alkali-metals, ammonium, alkali-earths, tin, lead, zirconium, titanium, and uranium. The interfering anions are fluoride, sulphate, phosphate, nitrate, chloride, sulfur dioxide, sulfites, carbondioxide, carbonates, and organic acids.

Procedures were given for an oxalic acid separation and the determination of thorium with APANS.

#### 1957

29. Fritz, J. S., Yamamura, S. S. and Richard, M. J., "Titration of Sulfate Following Separation with Alumina," Anal. Chem., 29, 158 (1957).

In acid solution it is possible to separate as little as 0.5 ppm. sulfate from large quantities of chloride, nitrate, and perchlorate, and from most metal ions by adsorption of the sulfate on a column of alumina. Two interfering ions which are also adsorbed are fluoride and phosphate ions. These must be absent or accounted for in the determination. Some metal such as zirconium(IV), chromium(III) or thorium(IV) may be separated from the sulfate by complexation with EDTA. This method of complexation sometimes fails because the EDTA complex may be broken up in the alumina column. The sulfate is eluted with dilute ammonium hydroxide, passed through a small cation exchange column and titrated with 0.01M. barium perchlorate. Thorin was used as the indicator.

Small amounts of sulfate in metal salts can be determined except where the metal ion forms a slow-reacting sulfate complex. The alumina column is also

used with a peroxide-bomb combustion to determine sulfur in a wide variety of organic compounds, with an error of 1% or less.

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